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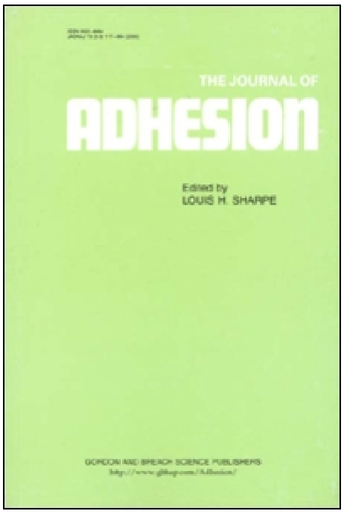

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Synergetic Effect of Grit-Blasting and Atmospheric Cold Plasma Pretreatments on the Surface Free Energy of a Fibreglass/Epoxy Vinyl Ester Composite

Danick Gallant[a]
[a] Structural Adhesives and Corrosion Group, Aluminium Technology Centre, Industrial Materials Institute, National Research Council Canada (ATC/IMI/NRC), Saguenay, Quebec, Canada

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Danick Gallant
Structural Adhesives and Corrosion Group, Aluminium Technology Centre, Industrial Materials Institute, National Research Council Canada (ATC/IMI/NRC), Saguenay, Quebec, Canada

For the first time, the efficiency of different surface pretreatment approaches prior to adhesive bonding of a fibreglass-reinforced epoxy vinyl ester thermoset composite has been investigated. It was found that grit-blasting generally had a negligible effect on the surface free energy (SFE) calculated using the Owens, Wendt, Rabel, and Kaelble method, as well as the Lifshitz–van der Waals/acid-base (LWAB) approach. However, contrary to abrading, grit-blasting has shown its efficiency to flatten sharp surface irregularities and introduce surface roughness features suitable to adhesive bonding processes. With or without a previous grit-blasting step, argon gas atmospheric cold plasma treatment has shown a slight to moderate efficiency in increasing the SFE polar component of the composite. However, it was found that the addition of 0.07% oxygen to the argon plasma readily allows an important gain in the SFE polar component. Indeed, when processed at a speed of 30 m/min on a previously grit-blasted composite surface, the Ar/O_2 *atmospheric cold plasma treatment increases the surface free energy to values* $>73\,mJ/m^2$*, making the surface condition optimized for structural adhesive bonding. An oxidation mechanism of the composite surface exposed to atmospheric cold plasma was suggested on the basis of correlations established between the polar part of SFE obtained from the Owens* et al. *method, acid/base components calculated using the LWAB approach, and ATR infrared spectroscopy signatures obtained for a model polyolefin material.*

Keywords: Atmospheric cold plasma; ATR-infrared spectroscopy; Epoxy vinyl ester thermoset composite; Grit-blasting; Optical microscopy; Owens and LWAB methods; Surface pretreatment

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Address correspondence to Danick Gallant, Structural Adhesives and Corrosion Group, Aluminium Technology Centre, Industrial Materials Institute, National Research Council Canada, 501 boulevard Université Est, Saguenay, Quebec, Canada, G7H 8C3. E-mail: danick.gallant@imi.cnrc-nrc.gc.ca

INTRODUCTION

Within the context of high energy costs and in response to increasing environmental concerns, the use of aluminium-composite hybrid structures represents, now more than ever, a promising way to decrease the weight of transportation vehicles such as buses and cars. Also, by bonding laminates to metal substrates, one can usually increase the flexural stiffness of a metal [1], making it highly suitable for a structural application within a vehicle. Because it allows dissimilar material assembly and uniformly distributed stresses between the joined parts, adhesive bonding is still the most suitable method to join together metallic and polymeric materials. However, as it is the case with metallic materials, most thermoset composites used for structural load-bearing applications require pre-bonding surface property modifications (physical and/or chemical).

For many years now, grit-blasting has been identified, by far, as the preferred surface pretreatment method for thermoset composites [2]. Indeed, because of their cross-linked structures and the intrinsic polarity of their resin polymer chains, thermoset composites are theoretically quite easy to bond. Hence, using a simple solvent degreasing step followed by a grit-blasting process, one can usually remove the mould release agent as well as the thin layer of low molecular weight species present on, or close to, the composite surface. The surface obtained, when properly roughened, presents a fresh molecular network that would readily interact with an adhesive. However, a certain number of surface free energy conditions must be present to ensure a strong and durable substrate-adhesive interaction. Indeed, based on Young's equation, it can be easily demonstrated that increasing the surface energy of a substrate to a value greater than the surface energy of an adhesive generally allows the latter to spread on the former. A more formal view of this phenomenon can be obtained from wettability envelopes.

According to Owens and collaborators [3,4], the surface free energy of a substrate (γ^S or SFE) can be divided into two components, *i.e.*, the polar part (γ^P) and the dispersive part (γ^D). While the dispersive component of γ^S mainly refers to weak van der Waals dispersive forces ($F \propto 1/r^6$), the polar component is commonly associated with all non-dispersive forces, namely permanent dipoles ($F \propto 1/r^3$) and dipole-induced dipole interactions, acid-base interactions, and hydrogen bonds (r is the distance that separates interacting entities) [5]. Therefore, when applying a surface pretreatment to increase the surface free energy of a substrate, one generally targets a significant increase in the polar part of γ^S. For example, it has been demonstrated that raising γ^P of a thermoplastic low-density polyethylene material

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increases the adhesive-substrate bond strength under the shear mode [6]. In this last example, the value of the γ^D component remained unaffected by the surface treatment.

Among the techniques able to significantly increase γ^P of a surface through the induction of polar chemical groups, atmospheric cold plasma technology is one of the most recent and promising experimental approaches. Indeed, since it operates under ambient pressure, it virtually presents no limitation in the size and shape of the parts to be treated. Moreover, keeping the integrity of the treated bulk material is not a concern, since the plasma temperature is low compared with traditional flame treatments. Therefore, overheating of the material is unlikely to occur. However, because they are inherently more difficult to bond, thermoplastic polymers [7] have been the object of most studies on the efficiency of atmospheric cold plasma as a surface pretreatment [*e.g.*, 6,8–13]. Consequently, there are no available data indicating to what extent atmospheric cold plasma can modify the surface free energy of a thermoset composite prior to adhesive bonding.

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Despite the recognized efficiency of grit-blasting as a pretreatment of thermoset composites prior to adhesive bonding, in a recent article, Boerio *et al.* reported that, up to date, only a few studies have quantitatively reported on the surface free energy modifications induced by grit-blasting processes [14]. Without being an extensive literature review, Table 1 presents to what extent grit-blasting typically influences surface free energy parameters measured for different thermoset composites. As shown, grit-blasting generally modifies both the γ^D and γ^P components of the surface free energy and, in all cases, the grit-blasting process led to a global increase of the surface free energy. Among available literature, the effect of grit-blasting on the surface free energy of epoxy-based composites has received more attention than any other thermoset resin. This interest is mainly explained by the importance of epoxy resins in the aerospace sector. However, because they are quite expensive, epoxy-based composites are generally not accessible to manufacturing industries such as automotive and bus businesses. In contrast, epoxy vinyl ester resin-based composites, due to their relatively low cost, acceptable mechanical strength, and resistance to moisture and chemical agents, would represent good candidates for the design of cost-effective hybrid aluminium-composite materials. Thus, they can be used as an alternative to polyester and epoxy resins in composite materials because their characteristics and strengths are inferior to epoxy, but superior to that of polyester.

Epoxy vinyl ester resins are produced by the esterification of an epoxy resin with an unsaturated monocarboxylic acid (*e.g.*, methacrylic acid). The general chemical structure of the epoxy vinyl ester prepolymer is

TABLE 1 Overview of the Surface Free Energy Calculated for Different Thermoset-Based Composites Before and After Grit-Blasting

		Surface energy (mJ/m^2)						
		Before grit-blasting			After grit-blasting			
Composite	Grit nature	γ^D	γ^P	γ^S	γ^D	γ^P	γ^S	Ref.
Bismaleimide resin/carbon fibres	150-grit silica	25.0	6.3	31.3	30.8	8.3	39.1	15
Epoxy resin/ graphite fibres	100-grit alumina	32	4	36	33	11	44	16
Epoxy resin/ graphite fibres (System #1)	220-grit white alumina	34.1	2.6	36.7	41.0	9.6	50.6	14
Epoxy resin/ graphite fibres (System #1)	220-grit garnet	34.1	2.6	36.7	29.2	22.0	51.2	14
Epoxy resin/ graphite fibres	220-grit white alumina	39.6	2.0	41.6	50.4	1.5	51.9	6
Polyester resin/ fibreglass	220-grit white alumina	42.7	1.5	44.2	54.6	1.6	56.2	6

presented in Fig. 1. Due to their chemical stability and steric hindrance, aromatic rings in the bisphenol A group provide resistance to chemicals similar to that of bisphenol-base epoxy resins. For their part, ester functions, susceptible to chemical attacks, are less numerous in epoxy vinyl ester resins than in polyester resins. This ratio makes epoxy vinyl ester resins more chemically stable than polyester resins. As far as the hydroxyl groups found in epoxy vinyl ester resins are concerned, they increase the chemical stability of a reinforced composite by improving the interface quality between the fibre and resin. Finally, unsaturations located at the end of prepolymer chains contribute to increasing the reactivity of C=C groups compared with C=C groups of polyesters which are located all along the prepolymer chain. This increased reactivity favours the polymerisation process.

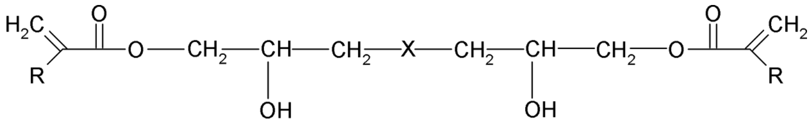

FIGURE 1 Chemical structure of a typical epoxy vinyl ester resin prepolymer, where R=H or CH_3 and X = bisphenol A or novolac group.

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Despite their interesting and promising overall properties for the design of adhesively bonded aluminium-composite hybrid structures, epoxy vinyl ester-based composites have not yet been the object of a study examining the influence of surface pretreatments on their surface free energy components. Therefore, the objective of this article is to highlight the effect of grit-blasting pretreatment on the surface free energy components of a fibreglass-reinforced epoxy vinyl ester composite. Also, since it represents a promising, versatile, high-speed, and dust-free surface treatment, emerging atmospheric cold plasma technology will be used individually or in combination with a grit-blasting process to advantageously modify the surface chemistry of the composite. Finally, a detailed discussion of the information provided, using a combination of surface free energy calculation methods, will be presented.

OVERVIEW OF TWO THEORETICAL APPROACHES FOR SURFACE FREE ENERGY QUANTIFICATION

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In 1963–1964, Fowkes introduced the concept of additivity of intramolecular forces [17,18] and, in the same way, pioneered the surface component approach. He suggested that the geometrical mean of the dispersion force components across an interface ($\sqrt{\gamma_S^D \gamma_L^D}$, where γ_S^D is the dispersion component of the surface and γ_L^D is the dispersion component of the liquid wetting the surface) is a measure of the interaction energy caused by dispersion forces, as long as only dispersion forces are involved:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S^D \gamma_L^D}.$$

Owens and Wendt [3], and Kaelble and Uy [4] included, in 1969 and 1970 respectively, the polar interactions to the theory suggested by Fowkes:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S^D \gamma_L^D} - 2\sqrt{\gamma_S^H \gamma_L^H},$$

where γ_S^H and γ_L^H represent hydrogen bonding terms for surface and liquid, respectively. The Owens *et al.* approach (sometimes called Kaelble method) then considers that both dispersive and non-dispersive interactions (*i.e.*, polar interactions) contribute to interactions across interfaces:

$$\gamma^S = \gamma^D + \gamma^P.$$

According to the Owens *et al.* theory, γ^D accounts for dispersive London interactions, while γ^P includes all of the non-dispersive forces, including H-bonding, acid-base, Keesom, and Debye energetic contributions [19]. As mentioned by Zenkiewicz, water and diiodomethane are the two most frequently used liquids to determine γ^{D} and γ^{P} parameters from the Owens *et al.* theory [20]. Because the drop shape analysis system available for contact angle measurements allows a third liquid, formamide was used as the second polar liquid. In the past, liquid triplet water-diiodomethane-formamide was successfully used for surface free energy measurements of different materials [*e.g.*, 20,21]. Moreover, as pointed out by Zenkiewicz, the SFE calculation method suggested by Owens *et al.* is the most often applied method for polymeric materials [20].

The Lifshitz–van der Waals/acid-base approach (LWAB) to determine the surface free energy of substrates was proposed by Good, Chaudhury, Fowkes, and Van Oss [22–27] some 20 years ago (sometimes called acid-base theory). This theory sustains that a noncovalent surface and interfacial interactions give rise to an apolar London–van der Waals component (γ^{LW}) and an acid-base component (γ^{AB}):

$$\gamma^{\mathrm{S}} = \gamma^{\mathrm{LW}} + \gamma^{\mathrm{AB}}.$$

While the γ^{D} parameter of the Owens *et al.* theory solely considers instantaneous dipole interactions associated with London forces, the γ^{LW} component takes into account London dispersion forces as well as Keesom (*i.e.*, dipole-dipole) and Debye (*i.e.*, dipole-induced dipole) interactions. On the other hand, acid-base interactions, that comprise two non-additive parameters, are the electron-acceptor (γ^{+}) and electron-donor (γ^{-}) surface tension parameters. The total acid-base contribution to the surface free energy, which also includes H-bonding interactions, is given by the following geometric mean:

$$\gamma^{\mathrm{AB}} = 2\sqrt{\gamma^{+}\gamma^{-}}.$$

Then,

$$\gamma^{\mathrm{S}} = \gamma^{\mathrm{LW}} + 2\sqrt{\gamma^{+}\gamma^{-}}.$$

This approach, from a theoretical point of view, is very interesting because it allows characterization of the acid-base character of the surface, in the sense of Lewis' definition of acidity and basicity. However, it is well known that the determined values of the components and, thus, the total surface free energy calculated according to the LWAB approach, depend strongly on the choice of the liquid triplet used [28,29]. Moreover, the arbitrary choice by Good and van Oss of equal values for the donor and acceptor parameters for water, *i.e.*, $\gamma^{+} = \gamma^{-} = 25.5\,\mathrm{mJ/m^2}$ [24], is still a controversy. Nevertheless, in the present article, surface free energy components determined using

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the liquid triplet water, diiodomethane, and formamide and by applying the Owens *et al.* and LWAB approaches, will be compared. Good has proposed to use apolar liquids 1-bromonaphtalene ($\gamma_L = 44.4\,\mathrm{mJ/m^2}$) and diiodomethane ($\gamma_L = 50.8\,\mathrm{mJ/m^2}$) for determination of the γ^{LW} component [22]. For the determination of γ^+ and γ^-, two polar liquids are required, and at least one of them must have equal basic and acidic parts. For this purpose, water ($\gamma^+ = \gamma^- = 25.5\,\mathrm{mJ/m^2}$) is used because it serves as a neutral point in the Lewis scale. Selection of the second polar liquid was done using the approach suggested by Holländer [30]. According to Holländer, the concept of mathematical instability must be considered to choose a pair of polar liquids. For each polar liquid, this study defines the ratio Qr, where:

$$\mathrm{Qr} = \gamma^-/\gamma^+.$$

The difference between two liquids can be calculated, giving ΔQr. For a liquid triplet containing one apolar liquid, the ΔQr parameter calculated for the two polar liquids should be as large as possible, indicating that the two polar liquids differ greatly in their Lewis acid/Lewis base characters. Combe *et al.* [31] have calculated the ΔQr value for 12 different liquid triplets. The largest ΔQr value, *i.e.*, 16.4, was obtained for liquid triplets containing water and formamide as polar liquids. According to Holländer, a value of 15 seems to be acceptable [30]. Therefore, formamide liquid selected for SFE calculations using the Owens *et al.* method is, according to Holländer's theory, also appropriate for SFE determination from the LWAB approach.

For accurate surface energy calculations, it is usually recommended to determine the effect of surface roughness on the measured contact angles. Indeed, contact angles measured for rough surfaces can be corrected to take into account the contribution of the roughness in the modification of the "real" contact angle, which is solely dependent on the energetic characteristics of the surface. Wenzel [32] defined a roughness correction factor (R_c) expressed as:

$$R_c = \frac{\cos(\theta_r)}{\cos(\theta_0)},$$

where θ_r is the contact angle made by a liquid with a rough surface and θ_0 is the contact angle made by the same liquid in the absence of roughness. In the present article, glycerol was used as a test liquid to calculate the roughness correction factor when required. In order to eliminate the effect of the surface chemistry on the roughness measurements, composites were previously coated for 30 seconds with a thin platinum film using a sputter coater operating at 150 mA. Although Dillingham and Oakley considered that the precision of surface free energy values for rough surfaces calculated with the Wenzel approach are suspect [33], this approach nevertheless represents a good way to establish surface free energy comparisons for the same material treated in different ways.

EXPERIMENTAL DETAILS

The main composite system used in this investigation was prepared using an epoxy vinyl ester resin obtained from Ashland Composite Polymers (Dublin, OH, USA). Details pertaining to the fibreglass content and composite moulding procedure cannot be revealed for proprietary reasons.

Grit-blasting procedures were performed using 220-grit high-purity ($\geq$99.3%) white alumina (White Abrasives, Niagara Falls, ON, Canada) and 220-grit HPX grade garnet particles (Barton Mines Company, Lake George, NY, USA). Oil-free compressed air was used for grit-blasting at a pressure of 80 psi (550 kPa). Two passes, at a 45° fixed approach angle and a 15-cm stand-off distance, were performed to obtain an appropriate level of roughness. Abrasion using a 24-grit aluminum oxide rotating pad (4" (10.2 cm) Metalite F226 resin fibre abrasive disc, from Norton Abrasives, Hamilton, ON, Canada) was also performed. This specific abrasion technique was used for comparison purposes with grit-blasting processes because it is usually easy to implement in industry and, more importantly, because it is often used for flattening of the whole surface of a composite. Prior to grit-blasting or abrading, samples were acetone degreased to minimize incorporation of surface impurities within the structural material.

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Plasma treatments were performed with an Atomflo$^{\mathrm{TM}}$-250 plasma source from Surfx$^{®}$ Technologies LLC (Culver City, CA, USA). The plasma was maintained by supplying a 13.56 MHz excitation RF to the electrodes [34]. Ar at a 30-L/min flow rate was used as primary gas, while O_2 at a 20-mL/min flow rate was sometimes used as secondary gas. The RF power was fixed at 80 W. The AH-250D plasma torch was precisely moved over the material's surfaces using a six-axis Motoman 3 kg payload robot (Yaskawa Motoman, Mississauga, ON, Canada). The plasma treatment speed ranged from 6 to 30 m/min, and samples were processed at a distance of $\sim$2 mm downstream of the showerhead. Prior to the plasma treatment, thermoset composites were degreased using acetone, abraded, or grit-blasted. Details regarding specific plasma treatment combinations with other surface pretreatments are given below in the appropriate sections.

Contact angles made by various liquids on the composite were measured on a KRÜSS DSA100 drop shape analysis system (Krüss USA, Matthews, NC, USA). The surface free energy (γ^{S} or SFE) of pretreated composites were calculated from the static contact angle of 2 μL sessile

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TABLE 2 Surface Free Energy Components of Liquids Used for Contact Angle Measurements

		Owens *et al.* theory		LWAB theory			
Liquid	γ^{S} (mJ/m^2)	γ^{D} (mJ/m^2)	γ^{P} (mJ/m^2)	γ^{LW} (mJ/m^2)	γ^{AB} (mJ/m^2)	γ^{+} (mJ/m^2)	γ^{-} (mJ/m^2)
Water	72.8	21.8	51.0	21.8	51.0	25.5	25.5
Formamide	58.0	39.0	19.0	39.0	19.0	2.28	39.6
Diiodomethane	50.8	50.8	0.0	50.8	0.0	0.0	0.0

drops (average of 6 drops for each liquid) of water, formamide, and diiodomethane used as probe liquids. The surface free energy components of these liquids are summarized in Table 2. Sufficient time was allowed for droplets to stop spreading before measuring contact angles, which were all carried out within 10 minutes after the surface pretreatment.

Surface roughness characterization of grit-blasted substrates was performed using an optical profilometer CHR450 from STIL (Sciences et Techniques Industrielles de la Lumière, Aix en Provence, France), used in conjunction with a field chromatic optical "pen." This instrument uses a high resolution non-contact sensor and allows examination of opaque and/or highly reflective surface finishes. This gave an overall z-axis resolution better than 0.03 μm. Stereomicroscope images were obtained from a Leica Model MZ16 microscope equipped with a camera (Leica Microsystems, Bannockburn, IL, USA) and XYZ motorized stage (Clemex Technologies Inc., Longueil, Canada). SEM images were obtained with a scanning electron microscope Hitachi model SU-70 using the secondary electron detection (Hitachi High-Technologies, Rexdale, ON, Canada).

The nature of chemical modifications induced on the surface of the composite during the atmospheric cold plasma treatment was studied using attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy. Spectra were obtained with a Nicolet 6700 (Thermo Scientific, Madison, WI, USA) on a horizontally mounted internal reflection element (single-reflection diamond crystal, refractive index of 2.4 at 1000 cm^{-1}, angle of incidence of 45°, 64 co-added scans with a spectral resolution of 4 cm^{-1}).

RESULTS AND DISCUSSION

Mechanical Pretreatments

The surface free energy of the fibreglass-reinforced epoxy vinyl ester composite was determined following a simple degreasing step using

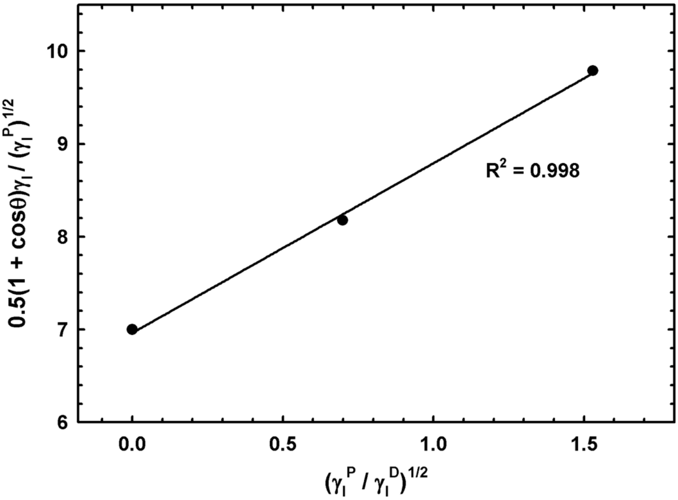

FIGURE 2 Linear Kaelble plot for acetone degreased fibreglass/epoxy vinyl ester composite.

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acetone with a Kimwipes^{TM} towel. Figure 2 presents the Kaelble plot made from contact angles measured for the liquids summarized in Table 2. Using the Owens *et al.* method, a total surface free energy of 51.8 mJ/m^2 ($\gamma^D = 48.5$ mJ/m^2; $\gamma^P = 3.3$ mJ/m^2) was determined for the degreased composite. By taking into account the roughness correction factor of 1.20 for that surface, a corrected surface free energy of 44.4 mJ/m^2 ($\gamma^D = 40.4$ mJ/m^2; $\gamma^P = 4.0$ mJ/m^2) was calculated, which is theoretically high enough to allow spreading of a two-component epoxy adhesive ($\gamma^D = 35$ mJ/m^2; $\gamma^P = 4$ mJ/m^2) on the surface of the composite [33]. Indeed, the wettability envelope calculated from these data demonstrates that the surface tension of the two-component epoxy adhesive lies inside the contour of the envelope defined by the corrected surface free energy of the degreased composite (figure not shown). From this point on, SFE values appearing in the text are corrected for surface roughness. Besides the basic information provided by wettability envelopes, Chin and Wightman [15] demonstrated that the durability of assemblies can be considerably improved by increasing the surface free energy of a composite to a higher level. In other words, the larger the difference between the surface tension of the adhesive and surface free energy of the composite is, the more durable the assembly can be. However, it is important to mention that, in some cases, increased interfacial surface free energy can promote dewetting by water [35]. A small polar component for the simply degreased

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surface was expected, since all surface impurities may not be completely soluble in acetone. Moreover, traces of impurities would also have remained strongly adsorbed within the first layers of the material, making them impossible to remove using a Kimwipes^{TM} towel. As shown in Table 1, polar components of the same order of magnitude were determined for different as-tooled composites. The surface free energy of the degreased composite was also determined using the LWAB theory. Results obtained ($\gamma^{S} = 44.1\,mJ/m^2$; $\gamma^{LW} = 41.4\,mJ/m^2$; $\gamma^{-} = 4.7\,mJ/m^2$; $\gamma^{+} = 0.4\,mJ/m^2$) are in accordance with those generated by the Owens *et al.* approach. Linearity observed on the Kaelble plot, as well as the closeness of the results obtained from the Owens *et al.* and LWAB theories, are indications of accurate results.

Figure 3a presents the surface morphology obtained from optical profilometry measurements performed on the acetone degreased fibreglass/epoxy vinyl ester composite. The vacuum moulding process employed leads to a rough surface on one side of the composite, and to a smooth and plane surface on the other side of the material. Since the smooth surface must be kept intact for aesthetic considerations (visible panels), only the rough surface shown in Fig. 3a should be considered for adhesive bonding (nevertheless, for comparison purposes only, Table 3 presents SFE calculated for the smooth side of the composite, degreased in one case and grit-blasted in the other). It is clearly shown in Fig. 3a that the moulding procedure employed to prepare the panels induces very sharp irregularities on the rough side of the composite. Consequently, flattening of the surface using a mechanical approach is required prior to bonding for two reasons. Firstly, these unflattened topographic features will lead to significant stress concentrations and, secondly, the chemistry of the surface is certainly different from the chemistry of the bulk resin material. Thus, with the aim of exposing the fresh bulk resin matrix, introducing reproducible surface roughness features, and removing the remaining traces of near-surface impurities, a grit-blasting process using 220-grit white alumina was performed. As shown in Fig. 3b, the grit-blasted substrate, at the presented scale, most likely exhibits a well defined pattern on a much smoother surface. Surface roughness from grit-blasting should help adhesion through a mechanical interlocking mechanism without creating stress concentrations due to voids that would otherwise be located between the adhesive and substrate [36]. Similar roughness features were observed on the surface of the grit-blasted composite using the garnet abrasive. As shown in Table 3, according to the Owens *et al.* approach, grit-blasting using 220-grit white alumina only allowed a negligible increase of the total surface free energy of the composite, *i.e.*, to 45.0 mJ/m^2, with dispersive and

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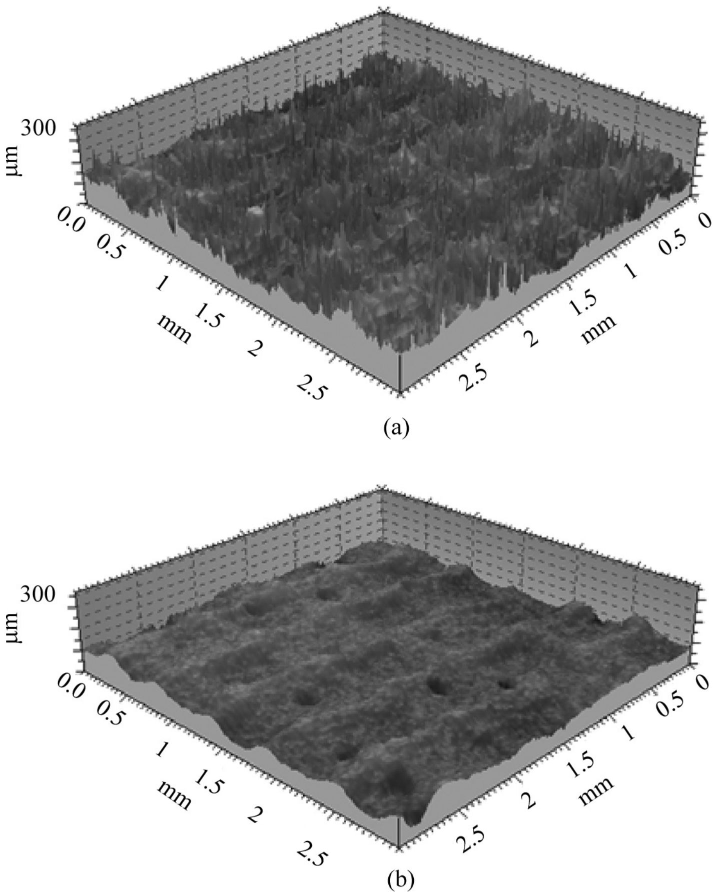

FIGURE 3 Optical profilometry images obtained on the fibreglass/epoxy vinyl ester composite: (a) degreased with acetone ($Ra = 25.4\,\mu m$); (b) grit-blasted with 220-grit white alumina ($Ra = 20.8\,\mu m$).

polar components being 41.2 and $3.8\,mJ/m^2$, respectively. Such SFE similarities with the only-degreased surface can be explained by the fact that the epoxy vinyl ester resin was cured without using an external heat supply and, moreover, the surface to bond was not pressed against a hot steel moulding plate. These results, and others obtained from mechanical pretreatments, are all summarized in Table 3. Contrary to white alumina, garnet abrasive was found to have a greater influence on the surface chemistry of the composite, since a $6.6\,mJ/m^2$ polar contribution was calculated using the Owens *et al.* approach ($\gamma^S = 46.5\,mJ/m^2$; $\gamma^D = 39.9\,mJ/m^2$). Results obtained from the LWAB theory are also in

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TABLE 3 Surface Free Energies Calculated for Mechanically Modified Fibreglass/Epoxy Vinyl Ester Composite Using Owens *et al.* and LWAB Approaches (Values Before Correction for Surface Roughness)

	Owens *et al.*			LWAB			
Surface treatment	γ^D (mJ/m^2)	γ^P (mJ/m^2)	γ^S (mJ/m^2)	γ^{LW} (mJ/m^2)	γ^- (mJ/m^2)	γ^+ (mJ/m^2)	γ^S (mJ/m^2)
Rough side: surface to bond							
Acetone degreased	40.4 (48.5)	4.0 (3.3)	44.4 (51.8)	41.4 (49.0)	4.7 (3.5)	0.4 (0.5)	44.1 (51.6)
Grit-blasting 220-grit white alumina	41.2 (50.4)	3.8 (2.9)	45.0 (53.3)	42.5 (50.8)	4.8 (2.9)	0.3 (0.5)	44.9 (53.2)
Grit-blasting 220-grit garnet	39.9 (48.3)	6.6 (6.6)	46.5 (54.9)	42.4 (50.8)	9.8 (9.3)	0.2 (0.3)	45.2 (54.1)
Abraded 24-grit pad	42.4 (50.6)	0.04 (0.6)	42.4 (51.2)	42.0 (49.1)	0.1 (1.3)	0.0 (0.0)	42.0 (49.1)
Smooth side: aesthetic surface							
Acetone degreased	41.0 (41.0)	1.4 (1.4)	42.4 (42.4)	42.8 (42.8)	2.7 (2.7)	0.0 (0.0)	42.8 (42.8)
Grit-blasting 220-grit white alumina	41.3 (46.7)	3.5 (3.1)	44.8 (49.8)	41.9 (46.9)	3.8 (2.9)	0.5 (0.6)	44.6 (49.5)

agreement with this value. In a recent paper, Boerio *et al.* found that for some epoxy-based composites, garnet abrasive leads to a significant increase of the SFE polar component [14]. Within a manufacturing environment, the use of garnet abrasives is advantageous, since it is a low-dust material and less expensive than white alumina.

The moulding/curing process of the epoxy vinyl ester resin employed leads to the formation of a macro-rough surface on one side of the panel. However, using a 24-grit abrading pad, it is possible to rapidly flatten the whole surface of the composite. This flattening procedure allows a fast rectification of the surface that could be required for some applications in which planarity is a requirement. To assess if this type of surface preparation gives a surface appropriate for adhesive bonding, surface free energy measurements were performed on it. Table 3 shows that a total SFE of $42.4\,\mathrm{mJ/m^2}$ was calculated, which is in quite good agreement with the values obtained from the other mechanical surface pretreatments that underwent assessment. However, a very low $0.04\,\mathrm{mJ/m^2}$ polar contribution characterizes this surface, making it highly hydrophobic in appearance. Indeed, a 105° water contact angle was measured for this surface, while a typical 65–75° contact angle was obtained following grit-blasting processes. This high contact angle may be explained by the presence of damaged fibres that tend to pin the advancing drop edge. Moreover, a heat build-up during the sanding process could have also lead to a modification of the composite's surface chemistry. Following the sanding process, because both the matrix and reinforcement fibres become exposed, it is difficult to distinguish which of these more importantly influences the observed hydrophobic behaviour. A stereomicroscopic investigation of this surface was done with the aim of attributing the hydrophobic character of the surface to distinct structures. Figure 4a presents a stereomicroscopic image obtained from the 24-grit abraded surface. It is clearly seen that this specific abrasion technique significantly exposes glass fibres contained in the composite (these glass fibres were not easily visible by eye). As presented on the SEM image in Fig. 4b, these fibres are loosely retained on the surface of the composite, which should be highly detrimental to adhesion. Although it is less demanding in dust control installations than grit-blasting, the pad abrasion technique also presents several processing issues, including the difficulty to manually control the applied pressure on the abrasive pad when automation is not a possibility. Because of this limitation, using a smaller grit does not represent an alternative, since it would have also probably led to the observation of uncovered and loosely retained fibres. Images presented in Figs. 4c and 4d confirm that grit-blasting allows observation of exposed but

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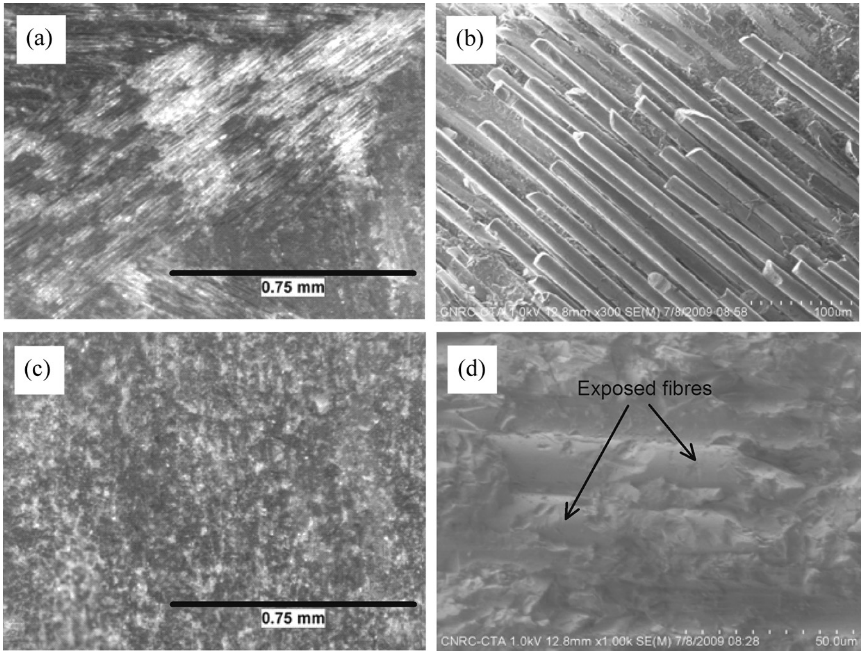

FIGURE 4 Stereomicroscopic and SEM images of the fibreglass/epoxy vinyl ester composite mechanically treated using: (a,b) 24-grit abrasive pad; (c,d) 220-grit white alumina.

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strongly retained fibres on the surface of the composite. Hart-Smith *et al.* [2] presented a similar exposition level for carbon fibres embedded within a carbon-epoxy laminate following a grit-blasting procedure considered as optimal for adhesive bonding.

Atmospheric Cold Plasma Pretreatments

Atmospheric cold plasma technology was used to induce chemical changes favourable to adhesion on the surface of the epoxy vinyl ester composite. The plasma shower was expected to be reactive enough to incorporate polar groups within the epoxy vinyl ester polymer chain. In previous years, low-pressure O_2 plasma has often been used to perform surface oxidation of different thermoset composites. Chin and Wightman [15] demonstrated that a 5-minute oxygen plasma exposition increases the surface free energy of a bismaleimide composite to a level of $78.7\,\mathrm{mJ/m^2}$ ($\gamma^{D} = 36.4\,\mathrm{mJ/m^2}$; $\gamma^{P} = 42.3\,\mathrm{mJ/m^2}$). Because it exceeds the surface tension of water, the SFE of the bismaleimide composite was determined using the Carre and Schultz method [35,37] that implies immersion of the composite in a liquid phase (instead of air). In a recent study published by Boerio *et al.* [14], a 30-second low-pressure O_2 plasma raised the SFE of a carbon fibre/epoxy composite to a value of 49.1 mJ/m^2 ($\gamma^D = 29.0$ mJ/m^2; $\gamma^P = 20.1$ mJ/m^2). However, it appears that low-pressure oxygen plasma is not very convenient for the pretreatment of large parts. Moreover, the relatively long duration of the treatment, as well as the time required to reach the low operating pressure inside the vacuum chamber, represent unacceptable limitations within a manufacturing context. For that reason, we investigated the efficiency of emerging atmospheric cold plasma technology equipped with a torch that is moved over the material's surface using a six-axis robot. Therefore, using this setup, there is virtually no limitation regarding the size and shape of the parts to be treated under atmospheric pressure conditions.

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An acetone degreased fibreglass/epoxy vinyl ester composite was treated using a 30 L/min argon plasma operated at a 6 m/min processing speed over the material's surface. The whole set of experimental parameters associated with the plasma treatment is given above in the Experimental Details section. Contact angle measurements performed on the as-processed part showed that argon plasma does not considerably influence the SFE of the composite, since values of 38.6, 6.2, and 44.8 mJ/m^2 were obtained for γ^D, γ^P, and γ^S, respectively. SFE components calculated using the LWAB approach ($\gamma^{LW} = 40.4$ mJ/m^2; $\gamma^{AB} = 3.6$ mJ/m^2; $\gamma^S = 44.0$ mJ/m^2) are highly consistent with results obtained from the Owens *et al.* method. These results, and others obtained for the composite submitted to atmospheric cold plasma treatments, are summarized in Table 4. In order to increase the oxidizing power of the plasma shower, a small concentration of oxygen was added to the argon gas. Wettability measurements demonstrated that the addition of 20 mL/min oxygen to a 30 L/min argon plasma (0.07% O_2 in Ar) significantly increases the SFE of the fibreglass/epoxy vinyl ester composite up to 59.6 mJ/m^2 ($\gamma^D = 34.9$ mJ/m^2; $\gamma^P = 24.7$ mJ/m^2), at a 6 m/min processing speed. Increasing the processing speed to 18 m/min slightly decreases the SFE obtained for the composite to 58.8 mJ/m^2 ($\gamma^D = 37.0$ mJ/m^2; $\gamma^P = 21.3$ mJ/m^2). Finally, using a processing speed comparable with those employed for flame treatment of polyolefin materials, *i.e.*, 30 m/min [38], the SFE is lowered to 50.3 mJ/m^2 ($\gamma^D = 37.4$ mJ/m^2; $\gamma^P = 12.9$ mJ/m^2). Therefore, it seems that the speed at which the Ar/O_2 plasma treatment is processed on the simply degreased composite significantly influences its efficiency. Moreover, when the processing speed exceeds approx. 20 m/min, an

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TABLE 4 Surface Free Energies Calculated for Fibreglass/Epoxy Vinyl Ester Composite Pretreated Using Atmospheric Cold Plasma Technology (Values Before Correction for Surface Roughness)

	Owens et al.			LWAB			
Surface treatment	γ^{D} (mJ/m^2)	γ^{P} (mJ/m^2)	γ^{S} (mJ/m^2)	γ^{LW} (mJ/m^2)	γ^{-} (mJ/m^2)	γ^{+} (mJ/m^2)	γ^{S} (mJ/m^2)
Ar 30 L/min; 6 m/min	38.6 (46.4)	6.2 (5.9)	44.8 (52.3)	40.4 (47.7)	8.1 (7.0)	0.4 (0.6)	44.0 (51.8)
Ar 30 L/min + O_2 20 mL/min; 6 m/min	34.9 (41.3)	24.7 (29.2)	59.6 (70.5)	40.6 (48.0)	40.5 (47.5)	0.4 (0.5)	48.6 (57.7)
Ar 30 L/min + O_2 20 mL/min; 18 m/min	37.0 (44.2)	21.3 (24.9)	58.8 (69.1)	42.5 (50.6)	35.0 (40.4)	0.3 (0.4)	49.0 (58.6)
Ar 30 L/min + O_2 20 mL/min; 30 m/min	37.4 (44.4)	12.9 (14.3)	50.3 (58.7)	40.2 (47.4)	17.7 (19.0)	0.7 (0.9)	47.2 (55.7)

important drop in the SFE polar component is noted. In Table 4, it is shown that, globally, γ^{D} values calculated using the Owens *et al.* method agree with γ^{LW} components calculated using the LWAB approach. This result is consistent with the fact that Keesom and Debye interactions are weak in the condensed phase compared with London forces [39]. However, as the value of the γ^{P} parameter increases, the total SFE calculated using the LWAB technique deviates from the SFE obtained from the Owens *et al.* approach. A tentative explanation of this phenomenon is advanced in the last section of this article.

Combined Mechanical and Atmospheric Cold Plasma Pretreatments

In previous sections, grit-blasting using either 220-grit alumina or garnet has shown its efficiency for the introduction of roughness features appropriate to adhesive bonding of a fibreglass/epoxy vinyl ester composite. Indeed, even though grit-blasting performed on the rough side of received panels does not importantly influence the SFE of the composite, it nevertheless smooths surface irregularities and then, minimizes probabilities of stress concentration to occur. On the other hand, it has been evidenced that the addition of 0.07% oxygen to argon cold plasma operating at atmospheric pressure markedly increases the SFE of an acetone degreased substrate to values around 60 mJ/m^2. However, when the plasma processing speed is increased to 30 m/min, min, an important drop in the SFE of the composite is observed compared with values calculated for lower processing speeds (*e.g.*, 6 m/min). Therefore, with the aim of favourably modifying both surface roughness and surface free energy of the substrate without decreasing the plasma processing speed in any way, combined grit-blasting and atmospheric cold plasma pretreatments were performed.

Following a grit-blasting step, the surface of a fibreglass/epoxy vinyl ester composite was treated using argon plasma at a processing speed of 18 m/min. From the Owens *et al.* method, a SFE of 47.6 mJ/m^2 ($\gamma^D = 41.4$ mJ/m^2; $\gamma^P = 6.2$ mJ/m^2) was calculated for the as-treated substrate. Such a value is comparable with those obtained for the composite treated using argon plasma, without any previous step of grit-blasting (see Table 4). This result clearly demonstrates that the action of argon plasma toward the freshly exposed epoxy vinyl ester resin matrix is not sufficient to increase the SFE of the composite to a higher level. In order to increase the ability of the argon plasma to modify the composite surface chemically when processed at a speed of 18 m/min, oxygen was again inserted into the argon gas. As shown in Table 5, the Ar/O_2 plasma torch, when operated at 18 m/min, increases the SFE of the alumina grit-blasted fibreglass/epoxy vinyl ester composite to a value >73 mJ/m^2. It then appears that the grit-blasting step makes the surface more reactive to the Ar/O_2 plasma by removing the contamination/inert layer of the material, or by activating the molecular network impacted by the particles (*e.g.*, by the generation of free radicals). However, because surface free energies of simply degreased and grit-blasted surfaces are almost equal, the decontamination theory is much more probable than the activation theory. Similar results were obtained at a 30 m/min treatment speed, and by replacing the alumina abrasive by the garnet material. These last surfaces had a 0° contact angle for water, diiodomethane, and formamide probe liquids. Therefore, a drop of water can be used as a qualitative probe for a fast quality assurance test of surface integrity prior to adhesive bonding. It is important to notice that because of its relatively high surface tension, water can rarely be used as probe liquid for the quality assessment of a thermoset composite. When the Ar/O_2 cold plasma treatment is processed at 18 m/min on a substrate previously abraded using a 24-grit pad, a 59.0 mJ/m^2 SFE ($\gamma^D = 33.9$ mJ/m^2; $\gamma^P = 25.1$ mJ/m^2) is obtained. Then, the presence of fibreglass reinforcement material on the surface of the composite adversely affects the apparent efficiency of atmospheric cold plasma

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TABLE 5 Surface Free Energies Calculated for Fibreglass/Epoxy Vinyl Ester Composite Pretreated Using a Mechanical Process Combined with Atmospheric Cold Plasma Technology (Values Before Correction for Surface Roughness)

Surface treatment										
	Plasma conditions			Owens *et al.* theory			LWAB theory			
Mechanical pretreatment	Ar (L/min)	O_2 (mL/min)	Processing speed (m/min)	γ^{D} (mJ/m^2)	γ^{P} (mJ/m^2)	γ^{S} (mJ/m^2)	γ^{LW} (mJ/m^2)	γ^{-} (mJ/m^2)	γ^{+} (mJ/m^2)	γ^{S} (mJ/m^2)
White alumina 220-grit	30	0	18	41.4 (50.4)	6.2 (5.9)	47.6 (56.3)	42.4 (50.8)	6.9 (5.7)	0.8 (1.1)	47.1 (55.8)
Garnet 220-grit	30	20	18	n/d	n/d	>73	n/d	n/d	n/d	>73
White alumina 220-grit	30	20	18	n/d	n/d	>73	n/d	n/d	n/d	>73
White alumina 220-grit	30	20	30	n/d	n/d	>73	n/d	n/d	n/d	>73
Abraded 24-grit	30	20	18	33.9 (39.4)	25.1 (29.4)	59.0 (68.8)	38.8 (44.9)	38.2 (44.1)	0.7 (0.9)	49.1 (57.5)

treatment. Indeed, because a significant fraction of the surface consists of exposed, fractured fibre material that does not respond to plasma treatment as does the epoxy vinyl ester resin, the measured magnitude of the effect is less, although the treatment level of the fraction that is exposed vinyl ester may be equivalent. Moreover, as previously pointed out, the presence of loosely retained fibreglass at the adhesive/composite interface is not recommended.

Correlation Between SFE Calculations From Owens et al. and Lifshitz–Van Der Waals/Acid-Base (LWAB) Methods

The Lifshitz–van der Waals/acid-base (LWAB) method to determine solid surface free energy, proposed by Van Oss and colleagues, presents a very useful approach, since it theoretically provides indications of the acid-base character of a surface. As mentioned previously, it is, however, the object of a controversy, since the assumption $\gamma^{+} = \gamma^{-} = 25.5\,\mathrm{mJ/m^2}$ for water does not seem to have a solid scientific base. On the other hand, the Owens *et al.* method has for a long time been used to quantify both dispersive and polar components of SFE. Strong bonds have been many times correlated to surfaces characterised by a high polar component calculated using the Owens *et al.* method. However, for both theoretical approaches, the choice of the probe liquids is still a challenge, especially when only three liquids are used.

Based on the probe liquid selection principle described by Holländer [30], water, diiodomethane, and formamide have been chosen to perform SFE measurements. Following each surface pretreatment, contact angle measurements were made and SFE calculated using the Owens *et al.* and LWAB approaches. Figure 5 presents correlations established between parameters γ^{AB} and γ^{P}, as well as between γ^{LW} and γ^{D}. All SFE calculations performed within the framework of this study were included in this graph, although they are not all reported in the tables. On the γ^{LW} *vs.* γ^{D} graph, a linear relationship between investigated parameters was found. Data points, almost all located inside the 99% confidence interval associated with the curve, demonstrate that the dispersive component of SFE calculated using the Owens *et al.* method generally agrees with the Lifshitz–van der Waals corresponding SFE parameter, determined from the LWAB theory. A quite good correlation between these two parameters was expected, since London forces are the main energetic contributors of both. On the other hand, on the γ^{AB} *vs.* γ^{P} plot in Fig. 5b, an exponential rise to a maximum curve better describes the general trend observed. In order to understand the physical significance of this curve shape, acid (γ^{+}) and base (γ^{-})

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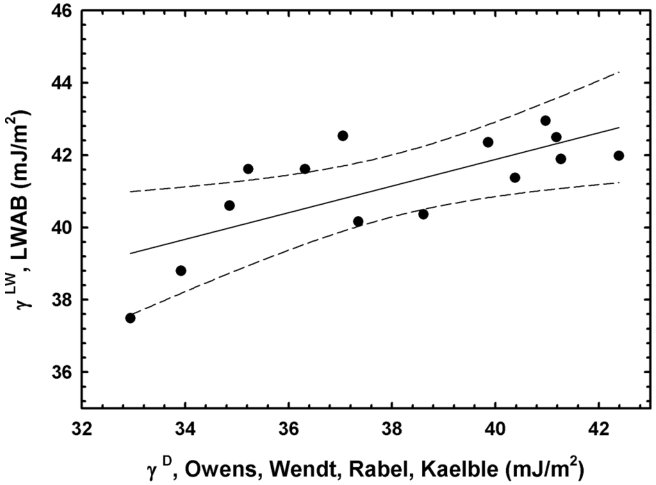
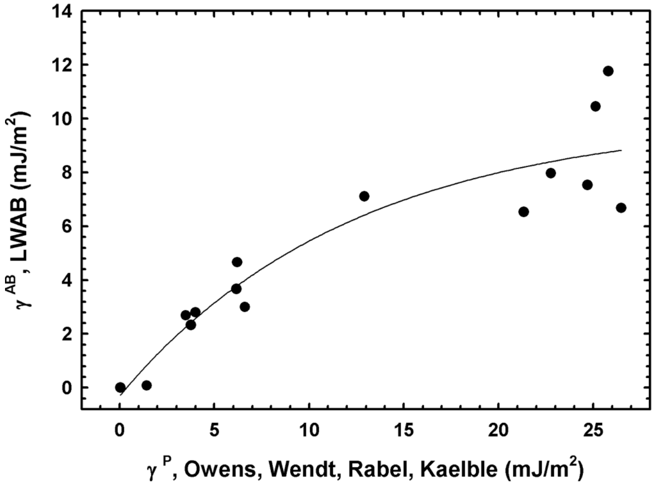


(a)



(b)

FIGURE 5 Relationship between (a) γ^{LW} and γ^{D}; (b) γ^{AB} and γ^{P} of SFE calculated using Owens *et al.* and LWAB theories (dashed lines: 99% confidence interval).

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components of the γ^{AB} parameter were independently plotted as a function of the γ^{P} parameter.

As presented in Fig. 6, while the γ^{+} parameter remains virtually unchanged when an important increase in γ^{P} is noted, the growth of

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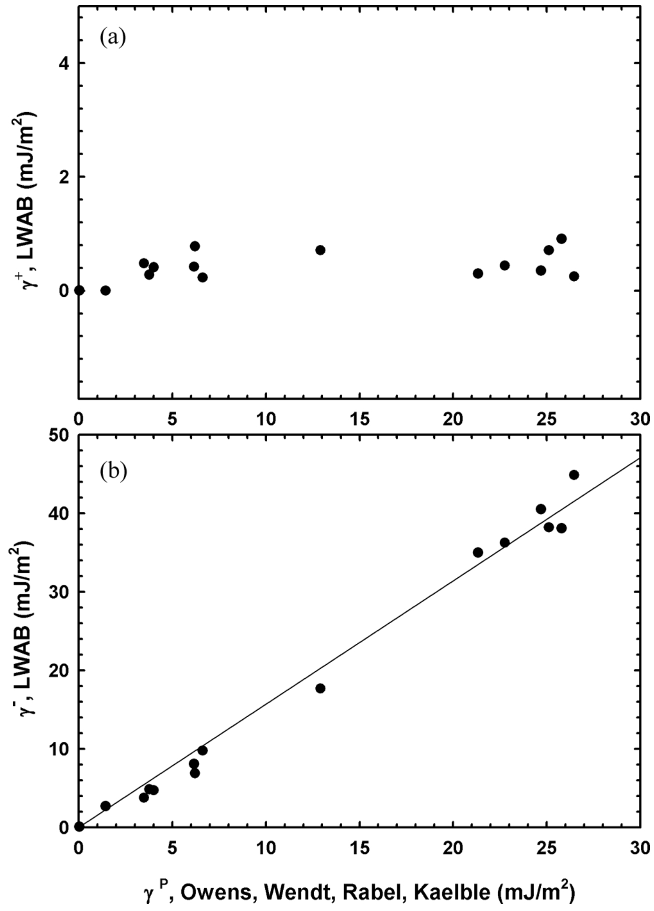

FIGURE 6 Variation of (a) acid, γ^+; (b) base, γ^- components of the γ^{AB} parameter as a function of the γ^P parameter.

γ^- is proportional to that of γ^P. Then, because γ^+ and γ^- are non-additive entities ($\gamma^{AB} = 2\sqrt{\gamma^+\gamma^-}$), an asymptotic behaviour is obtained in Fig. 5b. It is clearly seen in Fig. 6a that the acid character of the surface remains almost unaffected by either grit-blasting or atmospheric cold plasma treatments. On the other hand, Fig. 6b demonstrates that polar chemical functionalities induced on the surface of the fibreglass/epoxy vinyl ester composite (γ^P parameter) are directly related to the introduction of basic species on the surface, in the sense of Lewis' definition of acid-base (γ^-).

Lee *et al.* [40] have demonstrated using ESCA techniques that RF low-pressure O_2 plasma treatments performed on polypropylene introduce C=O, O–C=O, and C–O functionalities on the surface of the material. The formation under O_2 plasma of esters, alcohols, ethers, peroxides, and hydroperoxides has also been proposed [41]. In order to understand at a molecular-level the oxidation mechanism of the epoxy vinyl ester composite exposed to the atmospheric cold plasma shower, ATR infrared spectra of the composite surface were recorded. Figure 7a presents the ATR spectrum of the epoxy vinyl ester

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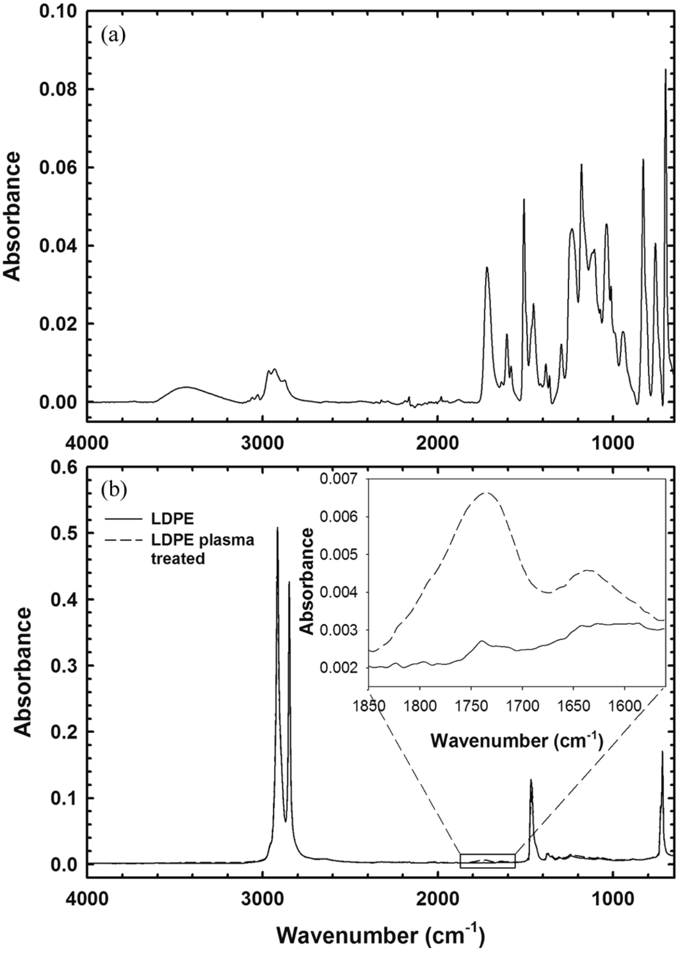

FIGURE 7 ATR infrared spectra of (a) Ar/O_2 plasma treated epoxy vinyl ester composite; (b) untreated and Ar/O_2 plasma-treated LDPE polymer.

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composite obtained following an Ar/O_2 plasma treatment. This spectrum does not allow observation of structural features specifically attributable to the plasma-treated composite. In fact, the strong carbonyl band located at 1718 cm^{-1} may overlay weaker –C=O absorption bands attributable to chemical functionalities introduced on the surface by the plasma treatment. Because oxidation of the composite at the aliphatic alkyl sites located all along polymer chains is likely, the nature of chemical changes inducible by the Ar/O_2 plasma treatment was studied on a low-density polyethylene (LDPE) polymer that does not contain any carbonyl groups. After having performed the plasma treatment at a low processing speed (*i.e.*, 0.3 m/min) on the LDPE substrate, the ATR spectrum was recorded on its surface.

Figure 7b shows spectra of the LDPE substrate, before and after plasma treatment. The spectral region 1850–1570 cm^{-1} shows absorption bands specifically attributable to the plasma treatment effect. As presented in Fig. 8, the deconvolution of this spectral region can be done using four Gaussian bands, namely anhydride antisymmetric (P1; 1789 cm^{-1}), anhydride symmetric (P2; 1761 cm^{-1}), ester (P3; 1733 cm^{-1}), and amide (P4; 1637 cm^{-1}) C=O stretching bands. According to the optimized deconvolution technique applied, the presence of carboxylic acid groups on the plasma oxidized surface is unlikely, since no carbonyl band was found in the spectral range 1710–1680 cm^{-1}. This last result is in agreement with surface free energy measurements performed on the epoxy vinyl ester composite that demonstrate

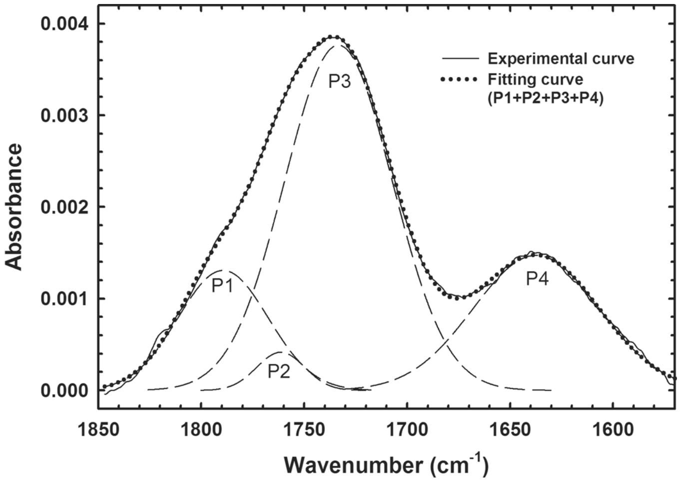

FIGURE 8 Deconvolution of the ATR infrared spectrum obtained for the Ar/O_2 plasma-treated LDPE polymer.

the major presence of Lewis base species (Fig. 6b) and a very weak contribution from Lewis acid groups (Fig. 6a). In the present case, by introducing O-containing species on the surface of the epoxy vinyl ester composite through probable radical-based catalyzed reactions with alkyl portions of the polymer chains, atmospheric cold plasma increases the surface concentration of electron rich systems (electron pair donors) which, in turn, increase the basic part of the polar surface free energy component. The relationship between γ^- and γ^P parameters, presented in Fig. 6b, supports this theory. Moreover, conditions under which the incorporation of oxygen-rich species on the surface of the composite occurs are clearly illustrated in Fig. 6. Indeed, in Figs. 6a and 6b, two sets of data are clearly distinguishable on both plots. The set of data located at $\gamma^P \geq 21\,\mathrm{mJ/m^2}$ is associated with Ar/O_2 atmospheric cold plasma pretreatments performed at low processing speeds on degreased surfaces only, and to high speed treatments practiced on previously grit-blasted surfaces. On the other hand, as far as the set of data at $\gamma^P < 7\,\mathrm{mJ/m^2}$ is concerned, it is related to grit-blasted surfaces and those pretreated using only argon gas in the atmospheric cold plasma. Thus, for the epoxy vinyl ester thermoset matrix, there exist clear relationships between pretreatment processing parameters (grit-blasted or not, plasma gas mixture, plasma processing speed), polarity of the surface, and its content in O-rich electron-donor species.

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CONCLUSION

The purpose of this article was to study the efficiency of grit-blasting and atmospheric cold plasma, used alone or in combination, for the pretreatment prior to bonding of a fibreglass/epoxy vinyl ester thermoset composite. It has been shown that grit-blasting does not have a significant effect on the surface free energy of the composite. However, by flattening surface irregularities induced by the moulding procedure of the panels, it provides surface roughness features appropriate to adhesive bonding. The further treatment of grit-blasted surfaces using an Ar/O_2 atmospheric cold plasma increases the SFE of the composite to values over $73\,\mathrm{mJ/m^2}$, even at a 30 m/min processing speed. Such an increase of the surface free energy was not achievable without performing a previous grit-blasting step that removes the surface contamination layers. Although abrasion using a 24-grit pad allows a rapid levelling of the rough composite surface, this process importantly exposes fibreglass, which could be detrimental to adhesion. Consequently, pad abrasion of the composite does not represent a promising surface pretreatment prior to adhesive bonding of the panels. The Lifshitz-van der Waals/acid-base (LWAB) approach is at the origin of important controversies, notably concerning values $\gamma^{+} = \gamma^{-} = 25.5\,\mathrm{mJ/m^2}$ arbitrarily attributed to water. Nevertheless, the present work has demonstrated that the liquid triplet water, diiodomethane, and formamide gives highly reliable results that are in good agreement with the surface free energy parameters calculated with the Owens *et al.* method. The reliability of these two SFE calculation approaches, combined with the ATR infrared spectroscopy analysis, permitted the proposal of an oxidation mechanism of the Ar/O_2 plasma-treated epoxy vinyl ester matrix, which takes place *via* the introduction of O-rich functional groups acting as Lewis bases. Because the combined grit-blasting and atmospheric cold plasma processes represent a robust surface pre-treatment, giving a SFE $>73\,\mathrm{mJ/m^2}$, water can be used as a probe liquid in a manufacturing environment for the quality assessment of the treated surface. By highlighting possibilities offered by combining a fast grit-blasting method with a high-speed versatile atmospheric cold plasma technique, this work represents a starting point toward a more extensive use of cost-effective epoxy vinyl ester-based composites within applications requiring structural adhesive bonding processes. Future work will soon be conducted to determine the influence of the surface pretreatment of the epoxy vinyl ester composite on the durability of aluminium-composite wedge assemblies.

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REFERENCES

[1] Jaguar Car Ltd., JAGUAR JNS 30.70.11, *Determination of Flexural Stiffness of Laminates Bonded to Metal Substrates*, (1994).

[2] Hart-Smith, L. J., Ochsner, R. W., and Radecky, R. L., *Engineered Materials Handbook: Adhesives and Sealants*, (ASM International, Materials Park, 1990), Vol. 3, pp. 840–844.

[3] Owens, D. K. and Wendt, R. C., *J. Appl. Polymer Sci.* **13**, 1741–1747 (1969).

[4] Kaelble, D. H. and Uy, K. C., *J. Adhesion* **2**, 50–60 (1970).

[5] Petrie, E. M., *Handbook of Adhesives and Sealants*, (McGraw-Hill, New York, 2007), 2nd ed., Ch. 2, pp. 39–58.

[6] Gallant, D., Eskandarian, M., and Arsenault, B., in *Proceedings of the 32nd Annual Meeting of The Adhesion Society, Inc.*, G. Anderson (Ed.) (The Adhesion Society, Blacksburg, VA, USA, 2009), pp. 308–310.

[7] Brewis, D. M., and Briggs, D., *Polymer* **22**, 7–16 (1981).

[8] Dillingham, R. G., Oakley, B. R., and Gilpin, D., *J. Adhesion* **84**, 1007–1022 (2008).

[9] Thurston, R. M., Clay, J. D., and Schulte, M. D., *J. Plastic Film Sheeting* **23**, 63–78 (2007).

[10] Stewart, R., Goodship, V., Guild, F., Green, M., and Farrow, J., *Int. J. Adhes. Adhes.* **25**, 93–99 (2005).

[11] Friedrich, J. F., Unger, W., Lippitz, W., Gross, T., Rohrer, P., Saur, W., Erdmann, J., and Gorsler, H.-V., *J. Adhes. Sci. Technol.* **9**, 569–586 (1995).

[12] Prat, R., Suwa, T., Kogoma, M., and Okazaki, S., *J. Adhesion* **66**, 163–182 (1998).

[13] Tsuchiya, Y., Akutu, K., and Iwata, A., *Prog. Org. Coat.* **34**, 100–107 (1998).

[14] Boerio, F. J., Roby, B., Dillingham, R. G., Bossi, R. H., and Crane, R. L., *J. Adhesion* **82**, 19–37 (2006).

[15] Chin, J. W. and Wightman, J. P., *Composites: Part A* **27A**, 419–428 (1996).

[16] Pocius, A. V. and Wenz, R. P., *Proc. 30th Natl. SAMPE Symp.* **30**, 1073–1087 (1985).

[17] Fowkes, F. M., *J. Phys. Chem.* **67**, 2538–2541 (1963).

[18] Fowkes, F. M., *Ind. Eng. Chem.* **56**, 40–52 (1964).

[19] Sharma, P. K. and Rao, K. H., *Adv. Colloid Interface Sci.* **98**, 341–463 (2002).

[20] Zenkiewicz, M., *Polym. Test.* **26**, 14–19 (2007).

[21] Zand, B. N. and Mahdavian, M., *Electrochim. Acta* **52**, 6438–6442 (2007).

[22] Good, R. J., *J. Adhes. Sci. Technol.* **6**, 1269–1302 (1992).

[23] Chaudhury, M. K., *Mater. Sci. Eng.* **R16**, 97–159 (1996).

[24] Good, R. J. and van Oss, C. J., The modern theory of contact angles and the hydrogen bond components of surface energies, in *Modern Approach of Wettability: Theory and Applications*, M. E. Schrader and G. Loeb (Eds.) (Plenum Press, New York, 1992), Ch. 1.

[25] Fowkes, F. M., *J. Adhes. Sci. Technol.* **1**, 7–27 (1987).

[26] van Oss, C. J., Good, R. J., and Chaundhury, M. K., *Langmuir* **4**, 884–891 (1988).

[27] van Oss, C. J., Chaundhury, M. K., and Good, R. J., *Adv. Colloid Interface Sci.* **28**, 35–64 (1987).

[28] Radelczuk, H., Holysz, L., and Chibowski, E., *J. Adhes. Sci. Technol.* **16**, 1547–1568 (2002).

[29] Cantin, S., Bouteau, M., Benhabib, F., and Perrot, F., *Colloids Surf. A: Physicochem. Eng. Aspects* **276**, 107–115 (2006).

[30] Holländer, A., *J. Colloid Interface Sci.* **169**, 493–496 (1995).

[31] Combe, E. C., Owen, B. A., and Hodges, J. S., *Dent. Mater.* **20**, 262–268 (2004).

[32] Wenzel, R. N., *Ind. Eng. Chem.* **28**, 988–994 (1936).

[33] Dillingham, R. G. and Oakley, B. R., *J. Adhesion* **82**, 407–426 (2006).

[34] Moravej, M., Yang, X., Nowling, G. R., Chang, J. P., Hicks, R. F., and Babayan, S. E., *J. Appl. Phys.* **96**, 7011–7017 (2004).

[35] Carre, A. and Schultz, J., *J. Adhesion* **15**, 151–161 (1983).

[36] Packham, D. E., Surface Roughness and Adhesion, in *Surfaces, Chemistry and Applications*, M. Chaudhury and A. V. Pocius (Eds.) (Elsevier, New York, 2002), 2nd ed., Ch. 7, pp. 317–349.

[37] Schultz, J., Tsutsumi, K., and Donnet, J.-B., *J. Colloid Interface Sci.* **59**, 272–276 (1977).

[38] Fourche, G., *Polym. Eng. Sci.* **35**, 968–975 (1995).

[39] Sun, C. and Berg, J. C., *Adv. Colloid Interface Sci.* **105**, 151–175 (2003).

[40] Lee, S. D., Sarmadi, M., Denes, F., and Shohet, J. L., *Plasma Polym.* **2**, 177–198 (1997).

[41] Hansen, G. P., Rushing, R. A., Warren, R. W., Kaplan, S. L., and Kolluri, O. S., Technical Paper AD89–537, Society of Manufacturing Engineers (1989).

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